Coating composition containing a non-halogen onium salt
Beschichtungszusammensetzung mit halogenfreiem Oniumsalz
Composition de revêtement contenant le sel d'onium exempt de halogène
Description

FIELD OF THE INVENTION

[0001] The present invention relates to a thermocurable coating composition which is suitable for an automotive top coating composition or a coil coating composition, and to a process for forming a cured film using the coating composition and to an article having the cured film thereon.

BACKGROUND OF THE INVENTION

[0002] A coating composition for top coating an automobile generally contains, as a film forming binder, a combination of a hydroxyl group-containing polymer and a melamine resin. The cured film obtained from the melamine curing system, however, has poor acid resistance and is damaged by acid rain which has recently become one of serious problems. The damage of the film provides poor appearance.

[0003] In order to overcome the above mentioned defects, the present inventors have proposed novel coating compositions without employing the melamine resin in Japanese Kokai Publications 45577/1990 and 287650/1991. The proposed coating compositions comprises a polymer having a carboxyl and carboxylate group derived by half-esterifying an anhydride group, and a polymer having an epoxy group or an epoxy and hydroxyl group. Since the composition cures by means of a reaction of the carboxyl group with the epoxy group as well as carboxylate group with hydroxyl group, and it forms a cross-linking point made of ester bond. Therefore, the resulting cured film has good acid resistance and sufficient weather resistance for an automotive top coating.

[0004] However, to achieve good acid and weather resistance, the cured film have to have high cross-linking density, and the coating composition for forming the cured film have to comprise a reactive resin of high functionality, and it becomes essentially poor in storage stability. Therefore, there has been a continued need for methods in order to impart excellent storage stability to the coating composition comprising a reactive resin of high functionality.

SUMMARY OF THE INVENTION

[0005] The present invention solves the problem above described, and the object is to provide a clear, solvent-borne coating composition having excellent curability and excellent storage stability, which provides a cured film having good weather resistance, particularly excellent acid resistance. The present invention also provides a process for forming a cured film and a coated article using the coating composition.

[0006] The present invention provides a liquid coating composition comprising:

(a) a compound having at least 2 carboxyl groups;

(b) a compound having at least 2 epoxy groups; and

(c) 0.01 to 3.0 parts by weight based on 100 parts by weight of the total resin solid of an onium salt.

[0007] The coating composition of the present invention is suitably used for a clear coating composition. The present coating composition is useful for coating any conventional coated or uncoated substrate. For example, the present coating composition may be employed for coating a pre-coated surface, as for what we call top coating composition. The pre-coated surface include, for example, a surface coated by cured or uncured solid colored film and a surface coated by cured or uncured composite film.

[0008] The present invention also provides a process for forming a cured film on a substrate comprising:

- priming and/or intercoating the substrate;
- applying a water-borne or solvent-borne color base paint to a primed and/or intercoated surface of the substrate;
- applying a clear solvent-borne coating composition to a base coated surface of the substrate without curing a base coating layer; and
- baking both the base coating layer and the clear coating layer to cure;

an improvement being present in that the clear coating composition comprises the coating composition described above.

DESCRIPTION OF THE INVENTION

[0009] The present invention provides a clear, solvent-borne liquid coating composition comprising:

(a) a compound having at least 2 carboxyl groups:
(b) a compound having at least 2 epoxy groups; and
(c) 0.01 to 3.0 parts by weight based on 100 parts by weight of the total resin solid of an onium salt as defined in
claim 1.

[0010] Preferably, the present coating composition further comprises 0.01 to 6.0 parts by weight based on 100 parts
by weight of the total resin solid of a metal salt of organic sulfonic acid (d).

[0011] The compound having at least 2 carboxyl groups (a) employed in the present coating composition is not
particularly limited, and may be any compound having an average of at least 2 carboxyl groups per molecule. Examples
of preferred polymer (a) include a polymer having carboxyl groups (a") which has an acid value of from 30 to 300
mgKOH/g solid and a number average molecular weight of 500 to 50000.

[0012] Preferred polymer (a") includes an acrylic polymer having carboxyl groups (a"1) and a polyester polymer
having carboxyl groups (a"2). The acrylic polymer having carboxyl groups (a") is particularly preferred, because the
resulting cured film has excellent weather resistance. The acrylic polymer having carboxyl groups (a"1) may be pre-
pared by copolymerizing 3.5 to 90%, preferably 7 to 60%, more preferably 10 to 50% by weight of an ethylenically
unsaturated monomer (Hereinafter, the wording "monomer" means "ethylenically unsaturated monomer") having a
carboxyl group (a")1(1), and 96.5 to 10%, preferably 93 to 40%, more preferably 90 to 50% by weight of a monomer
(a")1(4) which is different from (a")1(1). If the amount of the monomer (a")1 is less than 3.5% by weight, curability of
the resulting coating composition becomes poor, and if more than 90% by weight, the resulting cured film becomes
too hard and brittle and it provides poor weather resistance.

[0013] The copolymerization may be conducted by the usual solution polymerization, for example, under the condition
of normal or elevated pressure for 3 to 10 hours of reaction time at a temperature of 80 to 200°C by radical polymer-
ization initiated by azo compounds or peroxides in an amount of 0.5 to 15% by weight based on the total monomer
weight. In the polymerization, an additive, such as a chain transfer agent and an anti-oxidant may be employed.

[0014] Examples of the monomer having a carboxyl group (a")1(1) include acrylic acid, methacrylic acid, itaconic
acid and maleic acid and the like. These may be employed in alone or in combination of at least two.

[0015] Preferred monomer (a")1(1) is a long-chain monomer having a terminal carboxyl group (a")1(1) which contains
more than 6 carbon and/or oxygen atoms between an ethylenically unsaturated group and a carboxylic group. Such
a monomer may impart mar resistance to the resulting cured film.

[0016] The monomer (a")1(1) can be prepared, for example, by half-esterifying a monomer having a hydroxyl group
(a")1(2) of the formula:

wherein, R represents a hydrogen atom or a methyl group, X represents a linear or branched alkylene group having
2 to 8 carbon atoms, and Y represents an organic chain of the formula:

wherein, m represents an integer of 0 to 5, or of the formula:

R
The compound having an anhydride group employed in the present invention may be any compound which provides a carboxyl functionality by half-esterifying with a hydroxyl group under usual reaction condition such as a temperature of from room temperature to 150°C and normal pressures. The compound having an anhydride group has preferably 8 to 12, more preferably 8 to 10 carbon atoms, and preferably has saturated or unsaturated cyclic group, because such a compound may impart improved compatibility to the resulting polymer. Specific examples of the compound having an anhydride group include hexahydrophthalic anhydride, phthalic anhydride, 4-methylhexahydrophthalic anhydride, tetrahydrophthalic anhydride and trimellitic anhydride.

The half-esterification reaction is carried out according to any process known to the art, for example, at a temperature of from room temperature to 150°C. It is preferred in the reaction that an excess amount of the monomer having a hydroxyl group [a"1](2) is employed in order not to leave unreacted anhydride group.

The monomer [a"1](1)' may be employed in an amount of 3.5 to 90%, preferably 7 to 60% by weight, more preferably 10 to 50% by weight based on the total weight of monomers for the acrylic polymer having carboxylic group [a"1]. If the amount of the monomer [a"1](1)' is less than 3.5% by weight, curability of the resulting coating composition becomes poor, and if more than 90% by weight, flexibility of the resulting cured film may become poor.

The other preferred monomer [a"1](1) is an ethylenically unsaturated monomer having a carboxyl group and a carboxylate group, which is prepared by half-esterifying a monomer having an anhydride group [a"1](3) with a monoalcohol.

Specific examples of the monomer having an anhydride group [a"1](3) include itaconic anhydride, maleic anhydride and citraconic anhydride.

Typical examples of the monoalcohol include methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, n-hexyl alcohol, lauryl alcohol, methoxypropanol, acetol, allyl alcohol, propargyl alcohol and furfuryl alcohol. Dimethylamino ethanol, diethylamino ethanol, ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, ethylene glycol monononyl ether, polyalkylene glycol monoalkyl ether may also be employed.

The monomer [a"1](1) may be employed in an amount of 3.5 to 90%, preferably 7 to 60% by weight, more preferably 10 to 50% by weight based on the total weight of monomers for the acrylic polymer [a"1] component. If the amount of the monomer [a"1](1) is less than 3.5% by weight, curability of the resulting coating composition becomes poor, and if more than 90% by weight, the resulting cured film becomes too hard and brittle and it provides poor weather resistance.

The monomer [a"1](4) which is different from [a"1](1) may be any monomer which is compatible with a carboxylic group. For example, the monomer having a hydroxyl group [a"1](2) may be employed as the monomer [a"1](4).

For example, 5 to 90% by weight of the monomer having a carboxylic group [a"1](1), and 95 to 10% by weight of the monomer having hydroxyl group [a"1](2), and 0 to 60% by weight of the monomer [a"1](6) which is different from [a"1](1) and (a"1)(2) may be copolymerized to prepare a polymer having carboxyl groups and hydroxyl groups [a"1] which is particularly preferred for employing in the present coating composition.

The polymer [a"1] has an acid value of 30 to 300 mgKOH/g solid, preferably 60 to 180 mgKOH/g solid, a hydroxyl equivalent weight of 350 to 1200, preferably 400 to 1000, and an number average molecular weight of 1000 to 8000, preferably 1500 to 6000.

In preparation of the polymer [a"1], it is preferred to employ as the monomer [a"1](2), a long-chain monomer having a terminal hydroxyl group [a"1](2) which contains more than 6 carbon and/or oxygen atoms between an ethylenically unsaturated group and a hydroxyl group. Such a monomer may impart mar resistance to the resulting cured film.

Specific examples of the long-chain monomer having a terminal hydroxyl group [a"1](2) include 4-hydroxybutyl (meth)acrylate, an ε-caprolactone adduct of monomer [a"1](2) (for example, “Placcel FM-1”, “Placcel FA-1” and “Placcel FA-2” which are commercially available from Daicel Chemical Industries, Ltd), mono(meth)acrylate ester of polyethylene glycol, polypropylene glycol or 1,6-hexane diol.

The acrylic polymer having carboxylic groups [a"1] employed in the present invention may also be prepared by the method that copolymerizing the monomer having a hydroxyl group [a"1](2) and the monomer which is different from [a"1](2), and half-esterifying the resulting polymer with the compound having an anhydride group.

The acrylic polymer having carboxylic groups [a"1] employed in the present invention may also be prepared by the method that copolymerizing the monomer having an anhydride group [a"1](3) and a monomer [a"1](5) which is different from monomer [a"1](3), and half-esterifying the resulting polymer with a monoalcohol.

For example, a polymer having anhydride groups is prepared by copolymerizing 10 to 40% by weight of the monomer having an anhydride group [a"1](3) and 60 to 90% by weight of the monomer [a"1](5) which is different from
(a"1)(3). If the amount of the monomer (a"1)(3) is less than 10% by weight, curability of the resulting coating composition becomes poor, and if more than 40% by weight, the resulting cured film becomes too hard and brittle and it provides poor weather resistance.

[0033] The polymer having anhydride groups prepared by the copolymerization has preferably an average of at least 2 anhydride group per molecule, more preferably average 2 to 15 anhydride groups. If the number of the anhydride group is less than 2, curability of the resulting coating composition becomes poor, and if more than 15, the resulting cured film becomes too hard and brittle and it provides poor weather resistance.

[0034] The monomer (a"1)(5) which is different from (a"1)(3) may be any monomer which is compatible with the anhydride group.

[0035] An acrylic polymer having carboxyl groups and carboxylate groups (a"1) is then prepared by half-esterifying the resulting polymer with an excess amount of monoalcohol, preferably in an molar ratio of the the anhydride group to hydroxyl group of 1/10 to 1/1. If the molar ratio is more than 1, unreacted anhydride group remains into the composition and storage stability of the composition becomes poor.

[0036] Since half-esterification reaction may be conducted at lower temperature compared with polymerization reaction, the methods above described are useful when the compound having an anhydride group or a monoalcohol has low sublimation point or low boiling point.

[0037] The monoalcohol employed in the methods above described has 1 to 12, preferably 1 to 8 carbon atoms. These alcohols easily volatile upon heating, and conveniently regenerates an anhydride group. Typical examples of the monoalcohol include methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butyl alcohol, n-hexyl alcohol, methoxypropanol, dimethylamino ethanol, diethylamino ethanol, acetol, allyl alcohol, propargyl alcohol and furfuryl alcohol. Ethylene glycol monomethyl ether and ethylene glycol monooethyl ether may also be employed. Particularly preferred are methanol, ethanol, acetol, propargyl alcohol, allyl alcohol and furfuryl alcohol.

[0038] The acrylic polymer having carboxylic groups (a") employed in the present invention may be prepared by the method that copolymerizing the monomer having a carboxyl group (a") (1), the monomer having an anhydride group (a"1) (3) and a monomer (a") (7) which is different from (a") (1) and (a") (3), and half-esterifying the resulting polymer with a monoalcohol.

[0039] For example, an acrylic polymer having carboxyl groups and carboxylate groups (a") may be prepared by half-esterifying a polymer having anhydride groups which is prepared by copolymerizing 3.5 to 45% by weight of the monomer having a carboxyl group (a") (1), 10 to 40% by weight of the monomer having an anhydride group (a"1) (3) and remainder amount of the monomer (a") (7) which is different from (a") (1) and (a") (3), with a monoalcohol. In that case, the molar ratio of the anhydride group to the hydroxyl group of 1/10 to 1/1.

[0040] In preparation of the polymers, it is particularly preferred to employ a long-chain monomer having a terminal carboxyl group (a") (1) as the monomer (a") (1). Such a monomer may impart mar resistance to the resulting cured film.

[0041] The monomer (a") (4) which is different from (a") (1), the monomer (a") (5) which is different from (a") (3), the monomer (a") (6) which is different from (a") (1) and (a") (2) and the monomer (a") (7) which is different from (a") (1) and (a") (3) are not particularly limited. A monomer having one ethylenically unsaturation and 3 to 15, particularly preferred are methanol, ethanol, acetol, propargyl alcohol, allyl alcohol and furfuryl alcohol. Ethylene glycol monomethyl ether and ethylene glycol monooethyl ether may also be employed. Particularly preferred are methanol, ethanol, acetol, propargyl alcohol, allyl alcohol and furfuryl alcohol.

[0042] Specific examples of the monomer include (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth) acrylate and isobornyl (meth)acrylate; the monomer having a hydroxyl group (a") (2); styrene derivatives such as styrene, p-methylstyrene, p-t-butylstyrene, p-t-butylstylene; vinyl esters such as vinyl acetate, "Veova-9" and "Veova-10" available from Shell Chemical Co.; dimethylaminomethyl methacrylate; (meth)acyronitrile; and (meth)acrylamide. These may be employed in alone or in combination of at least two.

[0043] It is preferred that (meth)acrylates alone or a combination of at least 50% by weight of (meth)acrylates with the other monomer is employed as the monomer (a") (4) which is different from (a") (1), in order to improve durability and clarity of the cured film. When styrene or styrene derivatives are employed, an amount of not more than 40% by weight is preferred, in order to improve weather resistance of the cured film.

[0044] The acrylic polymer having carboxylic groups (a") preferably has an acid value of from 30 to 300 mgKOH/g solid, preferably 60 to 250 mgKOH/g solid, more preferably 90 to 200 mgKOH/g solid, number average molecular weight of from 500 to 50000, preferably 1000 to 20000, more preferably 1500 to 10000. If the acid value is less than 30 mgKOH/g solid, curability of the resulting coating composition becomes poor, and if more than 300 mgKOH/g solid, water resistance of the cured film becomes poor. If the molecular weight is less than 500, curability of the resulting composition becomes poor, and if more than 50000, viscosity of the resulting polymer becomes too high and workability becomes poor.

[0045] A combination of plurality of compounds having carboxylic groups (a") may be employed in the present coating composition.
Examples of the preferred is a combination of:

(a"") an acrylic polymer having carboxyl groups and carboxylate groups, and having an acid value of 30 to 250 mgKOH/g solid and number average molecular weight of 500 to 20000, wherein the polymer (a"") is prepared by half-esterifying the polymer having anhydride groups which is prepared by copolymerizing 10 to 40% by weight of a monomer having an anhydride group (a")(3) and 60 to 90% by weight of a monomer (a")(5) which is different from (a")(3), with a monoalcohol in a molar ratio of the anhydride group to the hydroxyl group of 1/10 to 1/1; with (a"") an acrylic polymer having carboxyl groups and hydroxyl groups, and having an acid value of 30 to 300 mgKOH/g solid, a hydroxyl equivalent weight of 350 to 1200 and a number average molecular weight of 1000 to 8000, wherein the polymer (a"") is prepared by copolymerizing 5 to 90% by weight of a monomer having a carboxyl group (a")(1), 95 to 10% by weight of a monomer having hydroxyl groups (a")(2) and 0 to 60% by weight of a monomer (a")(6) which is different from (a")(1) and (a")(2).

The other preferred examples of polymer having at least 2 carboxyl groups (a") include polyester polymer having at least 2 carboxyl groups (a'). The polyester polymer having carboxyl groups (a') may be prepared by condensing polybasic acid with polyhydric alcohol.

Examples of the polybasic acid include dibasic acids such as phthalic acid, isophthalic acid, terephthalic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, tetrahydrophthalic acid, hexahydrophthalic acid, maleic acid and fumaric acid; and anhydrides such as maleic anhydride, phthalic anhydride, succinic anhydride, tetrahydrophthalic anhydride, hemic anhydride, trimellitic anhydride, methylenebisxylene tricarboxylic anhydride and pyromellitic anhydride. Acid components other than polybasic acid such as acetic acid, 2-ethylhexanoic acid, benzoic acid, p-t-butylbenzoic acid and fatty acids may be employed for modification.

Examples of polyhydric alcohol include ethylene glycol, propylene glycol, 1,3-butanediol, glycerol, trimethylene glycol, dipropylene glycol, neopentyl glycol, hydroxypivalyl neopentyl glycol ester, hydrogenated bisphenol A, glycerol, trimethylol propane, trimethylol ethane, ditrimethylol propane, pentaerythritol and dipentaerythritol. A compound having epoxy group such as "Cardula E-10" (manufactured by Shell Chemical Co.) may also be employed in the same manner as the polyhydric alcohol.

The polymer (a") preferably has an acid value of from 30 to 300 mgKOH/g solid, preferably 60 to 260 mgKOH/g solid, more preferably 90 to 230 mgKOH/g solid, number average molecular weight of from 500 to 50000, preferably 600 to 10000, more preferably 700 to 6000. If the acid value is less than 30 mgKOH/g solid, water resistance of the cured film becomes poor. If the molecular weight is less than 500, curability of the resulting composition becomes poor, and if more than 50000, viscosity of the resulting polymer becomes too high and workability becomes poor.

A compound having at least 2 epoxy groups (b) employed in the present coating composition is not particularly limited, and may be any compound having an average of at least 2 epoxy groups per molecule.

Preferred compound (b) has 2 to 10, more preferably 3 to 8 epoxy groups per molecule, and has an epoxy equivalent weight of 280 to 900, more preferably 300 to 800. If the epoxy equivalent weight is more than 900, curability of the resulting coating composition becomes poor, and if less than 280, the resulting cured film becomes too hard and brittle and it provides poor weather resistance.

The compound (b) has a number average molecular weight of 500 to 50000, preferably 700 to 15000, more preferably 1000 to 6000. If the molecular weight is more than 50000, viscosity of the resulting polymer becomes too high and workability becomes poor, and if less than 500, curability of the resulting coating composition becomes poor.

Preferred compound (b) employed in the present coating composition is selected from the group consisting of an acrylic polymer having epoxy groups (b1), a glycidyl ether of polyhydric alcohol (b2) and a glycidyl ester of polybasic acid (b3). More preferably, the compound (b) is the acrylic polymer having at least 2 epoxy groups (b1).

The polymer (b1) may be prepared by copolymerizing 10 to 60% by weight of the monomer having an epoxy group (b1)(1) and 90 to 40% by weight of a monomer (b1)(3) which is different from (b1)(1) according to the procedure known to the art. If the amount of the monomer (b1)(1) is less than 10% by weight, curability of the resulting coating composition becomes poor, and if more than 60% by weight, the resulting cured film becomes too hard and brittle and it provides poor weather resistance.

Specific examples of the monomer having an epoxy group (b1)(1) include glycidyl (meth)acrylate, β-methylglycidyl (meth)acrylate and 3,4-epoxycyclohexylmethyl (meth)acrylate. In view of the balance of curability and storage stability, glycidyl (meth)acrylate is particularly preferred.

As the monomer (b1)(3) which is different from (b1)(1), the same monomer as the monomer (a")(4) which is described for preparing acrylic polymer having carboxyl groups (a") may be employed.
It is preferred that the monomer having a hydroxyl group (b1)(2) is employed as the monomer (b1)(3) to prepare an acrylic polymer having epoxy groups and hydroxyl groups (b1'). Adhesion of the resulting cured film may be improved by employing such a polymer. As the monomer (b1)(2), the same monomers which are described above as monomer (a"1)(2) are employed.

The monomer having a hydroxyl group (b1)(2) is preferably employed in an amount of from 5 to 60% by weight. If the amount is less than 5% by weight, the effect above described becomes poor, and if more than 60% by weight, compatibility of the resulting polymer becomes poor and reaction may progress incompletely. The polymer (b1') preferably has an average of 2 to 12, more preferably 4 to 10 hydroxyl groups per molecule.

The polymer (b1') has a hydroxyl equivalent weight of 280 to 1200, preferably 350 to 800 in addition to the epoxy equivalent weight above described. If the hydroxyl equivalent weight is less than 280, water resistance of the cured film becomes poor, and if more than 1200, the effect above described becomes poor.

The other preferred examples of the compound having at least 2 epoxy groups (b) include the glycidyl ether of polyhydric alcohol (b2) and a glycidyl ester of polybasic acid (b3). Examples thereof include glycerin triglycidyl ether, trimethylolpropane diglycidyl ether, trimethylolpropane triglycidyl ether, pentaerythritol pentaglycidyl ether, pentaerythritol triglycidyl ether, sorbitol hexaglycidyl ether and diglycidyl hexahydrophthalate ester. Among them, those having hydroxyl group therein such as trimethylolpropane diglycidyl ether and pentaerythritol triglycidyl ether are able to achieve the same effect as the acrylic polymer having epoxy groups and hydroxyl groups (b1').

In the present coating composition, the onium salt (c) and optionally the metal salt of organic sulfonic acid (d) are included in order to achieve the effect of excellent curability and storage stability.

The onium salt (c) may be employed in an amount of from 0.01 to 3 parts by weight, preferably 0.05 to 1.5 parts by weight, more preferably 0.1 to 1.2 parts by weight based on 100 parts of the total resin solid of the compound having at least 2 carboxyl groups (a) and the compound having at least 2 epoxy groups (b). If the amount of the onium salt (c) is less than 0.01 parts by weight, curability of the resulting coating composition becomes poor, and if more than 3.0 parts by weight, storage stability becomes poor.

The metal salt of organic sulfonic acid (d) may optionally be included in the present coating composition. It may be employed in an amount of from 0.01 to 6.0 parts by weight, preferably 0.05 to 4.0 parts by weight, more preferably 0.1 to 3.0 parts by weight based on 100 parts of the total resin solid of the compound having at least 2 carboxyl groups (a) and the compound having at least 2 epoxy groups (b). If the amount of the metal salt of organic sulfonic acid (d) is less than 0.01 parts by weight, storage stability of the composition becomes poor, and if more than 6.0 parts by weight, water resistance and weather resistance of the resulting cured film becomes poor and the film tend to become yellow.

The onium salt (c) is a compound of the formula:

\[ \text{[0068]} \quad \text{[II]} \]

wherein, Z represent a nitrogen atom or a phosphorus atom, R each independently represents an alkyl group having 1 to 20 carbon atoms, a cyclic alkyl group having 6 to 10 carbon atoms, an aryl group having 5 to 8 carbon atoms, an aralkyl group having 6 to 10 carbon atoms or a moiety which complete together with at least two of them a saturated or unsaturated heterocyclic ring comprising a nitrogen atom. R may have at least one halogen, nitrogen or oxygen atoms. \( \alpha \) represents an integer of 1 to 3.

X represents a nitrate ion, a nitrite ion, an acidic phosphate ion of the formula:
or a phosphonate ion of the formula:

\[
\begin{align*}
& (R - O -)_3 - n - P - ( - O H )_n \\
& (IV)
\end{align*}
\]

wherein, R represents each independently an alkyl group having 1 to 20 carbon atoms, preferably 2 to 12 carbon atoms, a cycloalkyl group having 6 to 10 carbon atoms, an aryl group having 5 to 8 carbon atoms or an aralkyl group having 6 to 10 carbon atoms. If the number of carbon atoms included by R is too small, water resistance of the resulting cured film becomes poor, and if too large, compatibility of the resulting polymer becomes poor. R may have at least one halogen, nitrogen or oxygen atoms. n represents 1 to 3.

Examples of a cationic part of the onium salt (c) include tetramethylammonium, tetraethylammonium, tetrapropylammonium, tetrabutylammonium, trimethylbenzylammonium, trimethylisobutylammonium, trimethylhexylammonium, trimethyldecylammonium, trimethyllaurylammonium, trimethylcetylammonium, trimethylstearylammonium, trimethylbenzylammonium, triethylbenzylammonium.

Examples of an anionic part of the onium salt (c) include nitrite, nitrate, methylphosphate, ethylphosphate, propylphosphate, butylphosphate, hexylphosphate, 2-ethylhexylphosphate, isodecylphosphate, laurylphosphate, phenylphosphate, dibutylphosphate, dihexylphosphate, di-2-ethylhexylphosphate, diilaurylphosphate, diphenylphosphate, butylphosphate, 2-ethylhexylphosphonate, dibutylphosphonate, di-2-ethylhexylphosphonate and o,o'-diethylphosphorodithioate.

The cationic part and the anionic part may be combined suitably to provide the onium salt (c) of the present invention. Specific examples of the onium salt (c) include tetrabutylammonium nitrate, tetrabutylammonium nitrite, tetrabutylammonium dibutylphosphate, trimethylbenzylammonium nitrate, trimethylbenzylammonium dibutylphosphate, trimethylbenzylammonium di-2-ethylhexylphosphate, trimethylcetylaminium dibutylphosphate, trimethylcetylaminium butylphosphonate, tetrabutylphosphonium dibutylphosphate, tetrabutylammonium di-2-ethylhexylphosphate, bis-trimethylbenzylaminium n-butylphosphate, trimethylcetylaminium 2-ethylhexylphosphate.

The onium salt (c) may be employed in alone or in combination of at least two.

It is essential to employ a nitrite ion, a nitrate ion, an acidic phosphate ion, or a phosphonate ion as the anionic part, in view of the balance between storage stability and curability of the coating composition.

The metal salt of organic sulfonic acid (d) is preferably a salt of an alkyl sulfonic acid or an alkyl substituted aromatic sulfonic acid with metal which is present in from the third to the fifth period and from II to VIII group of the periodic table.

For example, magnesium diparatoluenesulfonate, magnesium didodecylbenzenesulfonate, magnesium dinonylnaphthalenesulfonate, zinc diparatoluenesulfonate, zinc didodecylbenzenesulfonate, di-n-butyltin didodecylbenzenesulfonate and di-n-butyltin diparatoluenesulfonate. Particularly preferred are di-n-butyltin didodecylbenzenesulfonate, di-n-butyltin diparatoluenesulfonate, magnesium didodecylbenzenesulfonate, zinc didodecylbenzenesulfonate and tetrabutyldistannoxane didodecylbenzenesulfonate. These have good compatibility with resin, and stable in the coating composition.

The coating composition of the present invention is prepared by mixing the compound having at least 2 carboxyl groups (a); the compound having at least 2 epoxy groups (b); 0.01 to 3 parts by weight based on 100 parts of the total resin solid of the onium salt (c); and optionally 0.01 to 6.0 parts by weight based on 100 parts of the total resin solid of the metal salt of organic sulfonic acid (d).

The preparation may be made in such an amount that a molar ratio of the carboxyl group in the polymer (a) to the epoxy group in the polymer (b) is within the range of 1/1.2 to 1/0.6, preferably 1/1.1 to 1/0.8. If the compound (a) has carboxylate group and the compound (b) has hydroxyl groups, the composition preferably further satisfy the condition that a molar ratio of carboxylate group in the compound (a) to hydroxyl group in the compound (b) is within the range of 1/1.5 to 1/0.2, preferably 1/1.2 to 1/0.4.

If the molar ratio of the carboxyl group to the epoxy group is more than 1/0.6, curability of the resulting resin...
The above mentioned molar ratios can be specifically calculated by the methods known to the art from hydroxyl value, acid value and epoxy equivalent depending on the employed polymers.

It is preferred that the coating composition of the present invention contains 10 to 80%, preferably 30 to 70% by weight of the compound (a), and 20 to 90%, preferably 30 to 70% by weight of the compound (b). If the amount of the compound (a) is more than 80% by weight, the resulting cured film becomes too soft and acid resistance of the film becomes poor. If the amount is less than 10% by weight, mar resistance of the resulting cured film becomes poor.

The present coating composition may also contain melamine-formaldehyde resin and/or blocked isocyanate, in order to enhance crosslinking density and water resistance. Further, a UV absorber, a hindered amine light stabilizer and anti oxidant may be added to enhance weather resistance. The composition may also contain other additives, such as rheology controlling agent (e.g. crosslinked resin particles), surface controlling agent. In order to adjust viscosity of the resin composition, a diluent (e.g. alcohols, such as methanol, ethanol, propanol and butanol; hydrocarbon; esters) may be added thereto.

The resin composition has carboxyl groups which are neutralized with amine to make the composition water-dispersible or water-soluble. The resin composition may be formed into aqueous resin composition.

The coating composition of the present invention is suitably used for a clear coating composition. The present coating composition is useful for coating any conventional coated or uncoated substrate. For example, the present coating composition may be employed for coating a pre-coated surface, as what we call top coating composition. The pre-coated surface include, for example, a surface coated by cured or uncured solid colored film and a surface coated by cured or uncured composite film.

The clear coating composition is generally applied on a base coating layer formed from a base coating composition which is either aqueous or solvent-borne and contains color pigment. It is also preferred that the clear coating composition is applied on the base coating layer without curing the base coating layer and then the composite layer is baked to cure (two-coat one-bake curing system).

In case where the aqueous base coating composition is employed in the two-coat one-bake system, the base coating layer, if necessary, is heated at 60 to 100°C for 2 to 10 minutes before coating the clear coating composition. The base coating composition is generally explained in U.S. Patents 5,151,125 and 5,183,504 which are herein incorporated. Especially, the aqueous coating composition disclosed in U.S. Patent 5,183,504 is suitable in view of finish appearance and film performance.

The coating composition may be prepared by art-known methods, for example as enamel paint mixing ingredients by kneader or roll.

The resin composition may be applied on a substrate by spraying, brushing, dipping, roll coating, flow coating, rotary atomizing and the like. The substrate can be any one, including wood, metal, glass, fabric, plastics, plastic foam and the like. Preferred are plastics, metals (e.g. steel and aluminum) and alloys thereof. The substrate may be primed or intercoated by art-known methods if necessary.

The film thickness of the resulting coating layer may be varied depending upon its usage, but in many cases within the range of 20 to 100 µm.

The coated coating layer is generally cured by heating at a temperature of 100 to 180°C, preferably 120 to 160°C. Curing time may be varied by curing temperature, but generally for 10 to 30 minutes at a temperature of 120 to 160°C.

**EXAMPLES**

The present invention is illustrated by the following Examples which, however, are not to be construed as limiting the present invention to their details. The amounts expressed herein by "parts" or "%" is based on weight, unless otherwise indicated.

Preparative Example 1

A reaction vessel equipped with a thermometer, a stirrer, a cooling tube, a nitrogen inlet tube and a dropping funnel was charged with 360 parts of Arco Solve PMA (An organic solvent available from Kyowa Yuka K.K.), 777 parts of 4-hydroxybutyl acrylate, 820 parts of hexahydrophthalic anhydride and 0.48 parts of hydroquinone monomethyl ether. A temperature of the content was raised to 145°C and stirred over 20 minutes. The reaction mixture was then cooled and evacuated from the vessel to provide the monomer containing a carboxyl group i.

A reaction vessel equipped with a thermometer, a stirrer, a cooling tube, a nitrogen inlet tube and a dropping funnel was charged with 300 parts of xylene and 200 parts of Arco Solve PMA, and a temperature of the content was raised to 130°C. To the reaction vessel was dropwise added over 3 hours a solution of monomer and initiator consisting of 500 parts of the monomer containing a carboxyl group i, 100 parts of styrene, 200 parts of n-butyl acrylate and 50 parts of styrene.
parts of t-butyl-peroxy-2-ethylhexanoate. The content was stirred for 30 minutes at 130°C, and was dropwise added over 30 minutes a solution consisting of 10 parts of t-butyl-peroxy-2-ethylhexanoate and 100 parts of xylene. The content was stirred for 30 minutes at 130°C and cooled to provide a clear solution containing the acrylic polymer having carboxyl groups I, having a solid content of 50%. The resulting polymer I had a number average molecular weight of 4000 and an acid value of 108 mgKOH/g solid.

Preparative Example 2

[0094] A reaction vessel equipped with a thermometer, a stirrer, a cooling tube, a nitrogen inlet tube and a dropping funnel was charged with 80 parts of xylene and heated to 115°C. To the reaction vessel was dropwise added over 3 hours a solution of monomer and initiator consisting of 25 parts of styrene, 21 parts of n-butyl acrylate, 95 parts of n-butyl methacrylate, 34 parts of 2-ethylhexyl methacrylate, 50 parts of maleic anhydride, 100 parts of propylene glycol monomethyl ether acetate and 10 parts of t-butyl-peroxy-2-ethylhexanoate. The content was stirred for 2 hours and cooled to provide a clear solution containing the acrylic polymer having anhydride groups II, having a solid content of 53%. The resulting polymer II had a number average molecular weight of 5500.

[0095] A reaction vessel was added 415 parts of the resulting solution and 24.5 parts of methanol, and a temperature of the content was raised to 65°C and stirred for 24 hours to provide a clear solution containing the acrylic polymer having carboxyl groups and carboxylate groups II. An absorption due to an anhydride group (1785 cm⁻¹) was disappeared under analysis of infrared absorption spectra. The polymer II had an acid value of 127 mgKOH/g solid.

Preparative Example 3

[0096] A reaction vessel equipped with a thermometer, a stirrer, a cooling tube, a nitrogen inlet tube and a dropping funnel was charged with 400 parts of trimethylol propane, 130 parts of xylene and 123 parts of hexahydrophthalic anhydride. The content was stirred for 60 minutes at 130°C to provide a clear solution containing the polyester polymer having carboxyl groups III, having a solid content of 80% by weight. An absorption due to an anhydride group (1785 cm⁻¹) was disappeared under analysis of infrared absorption spectra. The polymer III had an acid value of 86 mgKOH/g solid.

Preparative Example 4

[0097] A reaction vessel equipped with a thermometer, a stirrer, a cooling tube, a nitrogen inlet tube and a dropping funnel was charged with 500 parts of butyl acetate and heated to 125°C. To the reaction vessel was dropwise added over 3 hours a solution of monomer and initiator consisting of 50 parts of styrene, 400 parts of glycidyl methacrylate, 350 parts of n-butyl methacrylate, 200 parts of 2-ethylhexyl acrylate and 70 parts of t-butyl-peroxy-2-ethylhexanoate. The content was stirred for 30 minutes at 125°C, and was dropwise added over 30 minutes a solution consisting of 10 parts of t-butyl-peroxy-2-ethylhexanoate and 250 parts of xylene. The content was stirred for 2 hours at 125°C and cooled to provide a clear solution containing the acrylic polymer having epoxy groups IV, having a solid content of 59%. The resulting polymer IV had a number average molecular weight of 4000 and an epoxy equivalent weight of 355.

Preparative Example 5

[0098] The acrylic polymer having hydroxyl groups and epoxy groups V were prepared according to the procedure described for preparative example 4, except using the ingredients tabulated in the following Table 1. Property of the resulting polymer is also indicated below.

<table>
<thead>
<tr>
<th>No. of obtained polymer</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precharged solvent (amount)</td>
<td>xylene (450) n-butanol (50)</td>
</tr>
<tr>
<td>Styrene</td>
<td>220</td>
</tr>
<tr>
<td>Glycidyl methacrylate</td>
<td>320</td>
</tr>
<tr>
<td>4-Hydroxybutyl methacrylate</td>
<td>220</td>
</tr>
<tr>
<td>2-Ethylhexyl acrylate</td>
<td>240</td>
</tr>
<tr>
<td>t-Butyl-peroxy-2-ethylhexanoate</td>
<td>50</td>
</tr>
<tr>
<td>Xylene</td>
<td>250</td>
</tr>
</tbody>
</table>
Preparative Example 6

[0099] The monomer having a carboxyl group vi were prepared according to the procedure described for preparative example 1, except using the ingredients tabulated at "monomer composition" in the following Table 2. The acrylic polymer having hydroxyl groups and carboxyl groups VI was then prepared using the compositions tabulated at "polymer composition" in the following Table 2. A clear solution containing the polymer VI, having a solid content of 57% was obtained. The resulting polymer VI had a number average molecular weight of 2100, an acid value of 100 mgKOH/g solid and a hydroxy equivalent weight of 560.

Preparative Example 7

[0100] A reaction vessel equipped with a thermometer, a stirrer, a cooling tube, a nitrogen inlet tube and a dropping funnel was charged with 700 parts of xylene and 500 parts by weight of "Solvesso 100" (An aromatic hydrocarbon solvent available from Exxon Chemical), and heated to 130°C. To the reaction vessel was dropwise added over 3 hours a solution of monomer and initiator consisting of 300 parts of styrene, 350 parts of 2-ethylhexyl acrylate, 150 parts of isobutyl methacrylate, 200 parts of acrylic acid, 150 parts of t-butyl-peroxy-2-ethylhexanoate and 300 parts of xylene. The content was stirred for 30 minutes at 130°C, and was dropwise added over 30 minutes a solution consisting of 20 parts of t-butyl-peroxy-2-ethylhexanoate and 20 parts of xylene. The content was stirred for 1 hours at 130°C and evaporated 1100 parts of solvent to provide a clear solution containing the acrylic polymer having carboxyl groups VII, having a solid content of 70%. The resulting polymer VII had a number average molecular weight of 1800 and an acid value of 156 mgKOH/g solid.

Preparative Example 8

[0101] A reaction vessel equipped with a thermometer, a stirrer, a nitrogen inlet tube, water separator and a condenser was charged with 210 parts of isophthalic acid, 370 parts of azelaic acid, 400 parts of trimethylol propane, 100 parts of neopentyl glycol, 50 parts of Cardula E, and was mildly heated to melt the contents. To the reaction vessel was then added 0.2 parts of dibutyltin oxide with stirring, and was heated to 220°C. With the proviso, in the temperature range
from 180 to 220°C, the reaction vessel was heated over 3 hours at a constant heating rate. The generated water was distilled out from the system. When the temperature reached 220°C, the reaction vessel was lagged for 1 hour, and to the reaction vessel was then slowly added 30 parts of xylene as a reflux solvent. The condensation reaction was continued in the presence of the solvent. When an acid value of the resin reached 10.0, the reaction vessel was cooled to 150°C, added 420 parts of phthalic anhydride, lagged for 1 hour, and cooled to 100°C. To the reaction vessel was added 275 parts of ethyl 3-ethoxypropionate and 275 parts of butyl acetate to provide a clear solution containing the polyester polymer having carboxyl groups VIII, having a solid content of 70%. The resulting polymer VIII had a number average molecular weight of 4200, a ratio of weight average molecular weight to number average molecular weight of 3.3, an acid value of 115 mgKOH/g solid.

Example 1 (for comparison)

[0102] A resin composition was prepared by mixing the ingredients tabulated in the following table 3.

[0103] The resulting resin composition was then diluted with a solvent mixture of butyl acetate and xylene (1/1) to a coatable viscosity to obtain a clear coating composition. Storage stability of the coating composition was then evaluated according to the following "Methods for Evaluation", and the results obtained are shown in Table 5.

[0104] A phosphated steel panel was coated with Power Top U-30 (Electrodeposition paint available from Nippon Paint Co., Ltd.) and Orga P-2 (Intercoating paint available from Nippon Paint Co., Ltd.). The intercoated panel was then base-coated with a solvent-borne metallic base paint (Super Lack M-90 available from Nippon Paint Co., Ltd.) and then further coated with the above obtained clear coating composition in the form of wet-on-wet. The clear coated panel was baked at 140°C for 30 minutes to obtain a cured film having a thickness of 40 µm.

[0105] The solvent-borne metallic base paint comprises 10.9 parts of aluminium pigment paste having an aluminium flake content of 65% ("Alpaste 7160N" available from Toyo Aluminium K.K.), 66.85 parts of thermocurable acrylic resin varnish having a solid content of 48% ("Almatex NT-U-448" available from Mitsui Toatsu Kagaku K.K.), 13.37 parts of melamine resin varnish having a solid content of 60% ("Uvan 20N-60" available from Mitsui Toatsu Kagaku K.K.), 6.38 parts of toluene, 2.0 parts of butanol and 0.5 parts of triethylamine.

[0106] The resulting cured film was evaluated as follows and the results obtained are shown in Table 5.

Methods for Evaluation

[0107] Storage stability: Viscosity of the coating composition was standardized to 30sec/20°C of Ford cup No.4. The coating composition was then stored for 10 days at 40°C. Viscosity of the stored coating composition was measured at 20°C by the use of Ford cup No.4 again. Increments of the viscosity represented by second was itself adopted as evaluation for storage stability of the coating composition.

[0108] Pencil hardness: The cured film was evaluated according to JIS K 5400-1979.

[0109] Warm water resistance: A cured film was dipped in warm water at 40°C for 10 days and then its appearance was observed by visual inspection according to the following criteria.

<table>
<thead>
<tr>
<th>No change</th>
<th>Slightly changed</th>
<th>Changed</th>
</tr>
</thead>
<tbody>
<tr>
<td>○</td>
<td>Δ</td>
<td>×</td>
</tr>
</tbody>
</table>

[0110] Acid resistance: The cured film was contacted with 0.2 ml of a 0.1 N H₂SO₄ aqueous solution at 60°C for 2 hours and then observed by visual inspection according to the following criteria.

<table>
<thead>
<tr>
<th>No change</th>
<th>Slightly changed</th>
<th>Changed</th>
<th>Definitely changed</th>
</tr>
</thead>
<tbody>
<tr>
<td>○</td>
<td>○</td>
<td>Δ</td>
<td>×</td>
</tr>
</tbody>
</table>

Examples 2 to 13 (for comparison)

[0111] Clear coating compositions were prepared as generally described in Example 1, except using the ingredients tabulated in the following Table 3, and the same evaluations as Example 1 were conducted. The results were shown in Table 5.
Examples 14

[0112] In place of the metallic base of the example 1, the intercoated panel was base-coated with a water-borne metallic base paint (The paint is described in Example 1 of U.S. Patent No. 5,183,504.). After drying at 60°C for 5 minutes, the panel was further coated with the clear coating composition of Example 1 in the form of wet-on-wet. The clear coated panel was baked at 140°C for 30 minutes to obtain a cured film having a thickness of 40 µm. The same evaluations as Example 1 were conducted for the cured film. The results were shown in Table 5.

[0113] The water-borne metallic base paint comprises 15 parts of aluminium pigment paste having an aluminium flake content of 65% ("Alpaste 7160N" available from Toyo Aluminium K.K.), 30 parts of methyled melamine ("Cymel 303" available from Cytec Ind. Inc.), 2 parts of isostearic phosphate ("Phosphorex A-180L available from Sakai Kagaku K.K."), 112 parts of acrylic resin varnish prepared in preparative example 1 of the U.S. Patent No. 5,183,504, having a number average molecular weight of 12000, a hydroxyl value of 70, an acid value of 58 and a solid content of 50%, and 43 parts of urethane emulsion having an acid value of 16.2 and a solid content of 33%.

Comparative Examples 1 to 4

[0114] A comparative clear coating composition was prepared as generally described in Example 1, except using the composition tabulated in the following Table 3, and the same evaluations as Example 1 were conducted. The results were shown in Table 5.
<table>
<thead>
<tr>
<th>Example no.</th>
<th>Polymers having</th>
<th>Curing catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COOH</td>
<td>COOH, COOR</td>
</tr>
<tr>
<td>1 for comparison</td>
<td>I</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 for comparison</td>
<td>II</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 for comparison</td>
<td>-</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>4 for comparison</td>
<td>-</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>5 for comparison</td>
<td>-</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>6 for comparison</td>
<td>I</td>
<td>-</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 for comparison</td>
<td>-</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>8 for comparison</td>
<td>-</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
</tr>
</tbody>
</table>

*1 Tetrabutylammonium bromide  
*2 Tetrabutylammonium salicylate  
*3 Magnesium didodecybenzenesulfonate  
*4 "Tinubin 900" available from Ciba Geigy A.G.  
*5 "Tinubin 123" available from Ciba Geigy A.G.  
*6 Tetrabutylphosphonium diethylphosphorodithioate
<table>
<thead>
<tr>
<th>Example no. for comparison</th>
<th>Polymers having COOH, COOH, OH, COOH epoxy group</th>
<th>Curing catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 for comparison</td>
<td>II, VI, V</td>
<td>TEPBr*7, MgDBS, T900, T123</td>
</tr>
<tr>
<td>-</td>
<td>200, 40, 210</td>
<td>1.0, 1.0, 3.0, 1.0</td>
</tr>
<tr>
<td>10 for comparison</td>
<td>II, VI, V</td>
<td>TBPBr*8, MgDBS, T900, T123</td>
</tr>
<tr>
<td>-</td>
<td>200, 40, 210</td>
<td>1.0, 1.0, 3.0, 1.0</td>
</tr>
<tr>
<td>11 for comparison</td>
<td>II, VI, V</td>
<td>TBPCl*9, MgDBS, T900, T123</td>
</tr>
<tr>
<td>-</td>
<td>200, 40, 210</td>
<td>1.0, 1.0, 3.0, 1.0</td>
</tr>
<tr>
<td>12 for comparison</td>
<td>II, VI, V</td>
<td>TBPPT, ZnDBS*10, T900, T123</td>
</tr>
<tr>
<td>-</td>
<td>200, 40, 210</td>
<td>1.0, 1.0, 3.0, 1.0</td>
</tr>
<tr>
<td>13 for comparison</td>
<td>II, VI, V</td>
<td>TBPPT, SnDBS*11, T900, T123</td>
</tr>
<tr>
<td>-</td>
<td>200, 40, 210</td>
<td>1.0, 1.0, 3.0, 1.0</td>
</tr>
<tr>
<td>Comp. 1</td>
<td>I, IV</td>
<td>TBABr, TBASA, T900, T123</td>
</tr>
<tr>
<td>200</td>
<td>115</td>
<td>0.3, 0.6, 2.0, 1.0</td>
</tr>
<tr>
<td>Comp. 2</td>
<td>II, V</td>
<td>TBPPT, T900, T123</td>
</tr>
<tr>
<td>-</td>
<td>200, 180</td>
<td>1.0, 2.0, 1.0</td>
</tr>
<tr>
<td>Comp. 3</td>
<td>II, VI, V</td>
<td>MgDBS, T900, T123</td>
</tr>
<tr>
<td>-</td>
<td>200, 40, 210</td>
<td>1.0, 3.0, 1.0</td>
</tr>
<tr>
<td>Comp. 4</td>
<td>II, VI, V</td>
<td>mgDBS, T900, T123</td>
</tr>
<tr>
<td>-</td>
<td>200, 40, 210</td>
<td>3.0, 1.0</td>
</tr>
</tbody>
</table>

*7 Tetraethylphosphonium bromide
*8 Tetrabutylphosphonium bromide
*9 Tetrabutylphosphonium chloride
*10 Zinc didodecylbenzenesulfonate
*11 Dibutyltin didodecylbenzenesulfonate
Example 15 to 27

[0115] Clear coating compositions were prepared as generally described in Example 1, except using the ingredients tabulated in the following Table 4, and the same evaluations as Example 1 were conducted. The results were shown in Table 5.
<table>
<thead>
<tr>
<th>Example no.</th>
<th>Polymer having</th>
<th>Curing catalysts</th>
<th>curing catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COOH</td>
<td>COOH, COOR</td>
<td>OH, COOH</td>
</tr>
<tr>
<td>15</td>
<td>VII</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>VII</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>VII</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>VII</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>-</td>
<td>II</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>II</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>II</td>
<td>-</td>
</tr>
</tbody>
</table>

*12 Tetrabutylammonium nitrate
*13 Tetrabutylammonium nitrite
*14 Tetrabutylammonium dibutylphosphate
*15 Trimethylbenzylammonium nitrate
*16 Tetramethylammonium dibutylphosphate
*17 Trimethylbenzylammonium dibutylphosphate
### Table 4 (continue)

<table>
<thead>
<tr>
<th>Example no.</th>
<th>Polymer having COOH, COOR, OH, COOH epoxy group</th>
<th>Curing catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>II</td>
<td>MBABP 1.0</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>SnDBS 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T900 T123</td>
</tr>
<tr>
<td>23</td>
<td>II V</td>
<td>MBAHP*18 0.5</td>
</tr>
<tr>
<td></td>
<td>200 40 210</td>
<td>SnDBS 2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T900 T123</td>
</tr>
<tr>
<td>24</td>
<td>II V</td>
<td>CABPA*19 0.5</td>
</tr>
<tr>
<td></td>
<td>200 40 210</td>
<td>T900 T123</td>
</tr>
<tr>
<td>25</td>
<td>II V</td>
<td>CABPN*20 0.5</td>
</tr>
<tr>
<td></td>
<td>200 40 210</td>
<td>T900 T123</td>
</tr>
<tr>
<td>26 for comparison VIII</td>
<td>II IV</td>
<td>TBPBP*21 0.5</td>
</tr>
<tr>
<td></td>
<td>45 100 75</td>
<td>T900 T123</td>
</tr>
<tr>
<td>27</td>
<td>VIII II</td>
<td>TMABP 0.5</td>
</tr>
<tr>
<td></td>
<td>45 100 75</td>
<td>MgDBS 2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T900 T123</td>
</tr>
</tbody>
</table>

*18 Trimethylbenzylammonium di-2-ethylhexylphosphate
*19 Trimethylcetylammomium dibutylphosphate
*20 Trimethylcetylammomium butylphosphonate
*21 Tetrabutylphosphonium dibutylphosphate
Table 5 shows that the coating compositions of examples 1 to 27 achieve excellent storage stability and excellent curability.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x</td>
<td>15.5</td>
<td>H</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>2 x</td>
<td>17.0</td>
<td>H</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>3 x</td>
<td>10.8</td>
<td>H</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>4 x</td>
<td>11.2</td>
<td>H</td>
<td>○</td>
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<td>5 x</td>
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<td>F</td>
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<td>○</td>
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<td>F</td>
<td>○</td>
<td>○</td>
</tr>
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<td>7 x</td>
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<td>HB</td>
<td>○</td>
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<td>8 x</td>
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<td>F</td>
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<td>○</td>
</tr>
<tr>
<td>9 x</td>
<td>11.8</td>
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* for comparison

[0116] Table 5 shows that the coating compositions of examples 1 to 27 achieve excellent storage stability and excellent curability.

Claims

1. A clear, solvent-borne coating composition comprising:

   (a) a compound having at least 2 carboxyl groups;
   (b) a compound having at least 2 epoxy groups; and
   (c) 0.01 to 3.0 parts by weight, based on 100 parts by weight of the total resin solids, of an onium salt represented by the formula:

   \[ [\text{N(R)}\text{4}]^{+}X^{-}\alpha \]

   wherein each R is independently selected from C\text{1-20} alkyl, C\text{6-10} cyclic alkyl, C\text{5-8} aryl and C\text{6-10} aralkyl, or two R’s together with the N atom form a saturated or unsaturated heterocyclic ring, and R may have at least one halogen,
nitrogen or oxygen atom; X represents a nitrite, nitrate, acidic phosphate or phosphonate ion; and a is an integer of 1 to 3.

2. A coating composition according to claim 1, wherein the compound having at least 2 carboxyl groups is a polymer having carboxyl groups, an acid value of 30 to 300 mg KOH/g solids, and a number average molecular weight of 500 to 50,000.

3. The coating composition according to claim 2, wherein the polymer having carboxyl groups is an acrylic or polyester polymer having carboxyl group, and the amount of this polymer in the coating composition is 10 to 80% by weight based on the total resin solids.

4. The coating composition according to claim 3, wherein the acrylic polymer having carboxyl groups is obtainable by copolymerising 3.5 to 90% by weight of a monomer having a carboxyl group and 96.5 to 10% by weight of another monomer.

5. The coating composition according to claim 4, wherein the monomer having a carboxyl group is a long-chain monomer having a terminal carboxyl group.

6. The coating composition according to claim 5, wherein the acrylic polymer having carboxyl groups is obtainable by copolymerising 5 to 90% by weight of a monomer having a carboxyl group, 95 to 10% by weight of a monomer having a hydroxyl group, and 0 to 60% by weight of a further monomer.

7. The coating composition according to claim 4, wherein the monomer having a carboxyl group is obtainable by half-esterifying a monomer having an anhydride group with a monoalcohol, wherein the molar ratio of the anhydride group to the hydroxyl group is 1/10 to 1/1.

8. The coating composition according to claim 3, wherein the acrylic polymer having carboxyl groups is obtainable by the steps of copolymerising 10 to 40% by weight of a monomer having an anhydride group and 60 to 85% by weight of different monomer, and half-esterifying the resultant polymer having anhydride groups with a monoalcohol, wherein the molar ratio of the anhydride group to the hydroxyl group is 1/10 to 1/1.

9. The coating composition according to claim 3, wherein the acrylic polymer having carboxyl groups is obtainable by the steps of copolymerising 3.5 to 45% by weight of a monomer having a carboxyl group, 10 to 40% by weight of a monomer having an anhydride group, and the balance of a further monomer, and half-esterifying the resultant polymer having anhydride groups with a monoalcohol, wherein the molar ratio of the anhydride group to the hydroxyl group is 1/10 to 1/1.

10. A coating composition comprising:

    20 to 80% by weight of a first polymer having carboxyl groups and carboxylate groups, an acid value of 30 to 300 mg KOH/g solids, and a number average molecular weight of 500 to 20,000, and which is obtainable by the steps of copolymerising 10 to 40% by weight of a monomer having an anhydride group and 60 to 90% by weight of another monomer, and half-esterifying the resultant polymer having anhydride groups with a monoalcohol, wherein the molar ratio of the anhydride group to the hydroxyl group is 1/10 to 1/1;

    20 to 80% by weight of a second polymer having carboxyl groups and hydroxyl groups, an acid value of 30 to 300 mg KOH/g solids, a hydroxyl equivalent weight of 350 to 1200 and a number average molecular weight of 1,000 to 8,000, and which is obtainable by copolymerising 5 to 90% by weight of a monomer having a carboxyl group, 95 to 10% by weight of a monomer having a hydroxyl group, and 0 to 60% by weight of a further monomer;

    a compound having at least 2 epoxy groups; and

    0.01 to 3.0 parts by weight, based on 100 parts by weight of the total resin solids, of an onium salt as defined in claim 1.

11. The coating composition according to claim 6 or claim 10, wherein the monomer having a carboxyl group is a long-chain monomer having a terminal carboxyl group, and the monomer having a hydroxyl group is a long-chain monomer having a terminal hydroxyl group.

12. The coating composition according to any one of claims 1 to 11, wherein the compound having at least 2 epoxy
groups has an epoxy equivalent weight of 280 to 900 and a number average molecular weight of 500 to 50,000.

13. The coating composition according to claim 12, wherein the compound having at least 2 epoxy groups is an acrylic polymer having epoxy groups, a glycidyl ether of a polyhydric alcohol or a glycidyl ester of a polybasic acid, and the amount of this compound in the composition is 20 to 80% by weight based on the total resin solids.

14. The coating composition according to claim 13, wherein the acrylic polymer having epoxy groups is obtainable by copolymerising 10 to 60% by weight of a monomer having an epoxy group and 90 to 40% by weight of another monomer.

15. The coating composition according to claim 13 or claim 14, wherein the acrylic polymer having epoxy groups also has hydroxyl groups, a epoxy equivalent weight of 280 to 900, a hydroxyl equivalent weight of 280 to 1200 and a number average molecular weight of 500 to 50,000, and wherein the acrylic polymer is obtainable by copolymerising 10 to 60% by weight of a monomer having an epoxy group, 5 to 60% by weight of a monomer having a hydroxyl group, and the balance of a further monomer.

16. The coating composition according to any of claims 1 to 15, wherein each R is independently C1-20 alkyl, C5-8 aryl or C6-10 aralkyl, and R may have at least one oxygen atom, and X- is an ion derived from an acidic phosphate or phosphonate of the formula

\[(R'O)_3-nPO(OH)_n\] or \[R'R'O-P(O)(OH)-R^+\]

wherein each R' is independently C1-20 alkyl, C6-10 cycloalkyl, C5-8 aryl or C6-10 aralkyl, and n is an integer of 1 to 3.

17. The coating composition according to any of claims 1 to 16, wherein the onium salt is selected from tetrabutylammonium dibutylphosphate, trimethylbenzylammonium dibutylphosphate, trimethylbenzylammonium dibutylphosphate, trimethylcetylammonium dibutylphosphate, trimethylcetylammonium dibutylphosphate, bis-trimethylbenzylammonium n-butylphosphate, and trimethylcetylammonium 2-ethylhexyolphosphate.

18. The coating composition according to any one of claims 1 to 17, wherein the compound having at least 2 epoxy groups is obtainable from a monomer selected from glycidyl (meth)acrylate and β-methylglycidyl (meth)acrylate.

19. The coating composition according to any of claims 1 to 9, wherein the compound having at least 2 carboxyl groups is

(i) an acrylic polymer obtainable from a monomer selected from glycidyl (meth)acrylate and β-methylglycidyl (meth)acrylate,
(ii) a glycidyl ether of polyhydric alcohol or
(iii) a glycidyl ester of polybasic acid.

20. A process for forming a cured film on a substrate, comprising:

- priming and/or intercoating a surface of the substrate;
- applying a water-borne or solvent-borne colour base paint to the primed and/or intercoated surface;
- applying a clear coating composition to the base-coated surface of the substrate, without curing the base layer; and
- baking, and curing, both the base layer and the clear coating layer;

wherein the clear coating composition comprises a coating composition according to any preceding claim.

**Patentansprüche**

1. Klare, Lösungsmittel-basierte Überzugszusammensetzung, umfassend:

   a) eine Verbindung mit mindestens 2 Carboxylgruppen;
b) eine Verbindung mit mindestens 2 Epoxigruppen; und
c) 0,01 bis 3,0 Gew.-Teile, bezogen auf 100 Gew.-Teile der gesamten Harzfeststoffe, eines Oniumsalzes der Formel:

\[ \left[N(R)_{10}\right]^{+}\alpha X^{\alpha-}, \]

worin jedes R unabhängig aus C_{1-20}-Alkyl-, C_{6-10}-Cycloalkyl, C_{5-8}-Aryl und aus C_{6-10}-Aralkyl ausgewählt ist, oder 2 Reste R zusammen mit dem N-Atom einen gesättigten oder ungesättigten heterocyclischen Ring bilden, wobei R mindestens ein Halogen-, Stickstoff- oder Sauerstoffatom aufweisen kann, und worin X ein Nitrit-, Nitrat-, saures Phosphat- oder Phosphonation darstellt und \( \alpha \) eine ganze Zahl von 1 bis 3 ist.

2. Überzugszusammensetzung gemäß Anspruch 1, worin die Verbindung mit mindestens 2 Carboxylgruppen ein Polymer mit Carboxylgruppen mit einem Säure-Wert von 30 bis 300 mg KOH/g Feststoffe und mit einem zahlen-
durchschnittlichen Molekulargewicht von 500 bis 50.000 ist.

3. Überzugszusammensetzung gemäß Anspruch 2, worin das Polymer mit Carboxylgruppen ein Acryl- oder Poly
esterpolymer mit Carboxylgruppen ist und die Menge dieses Polymers in der Überzugszusammensetzung 10 bis 80 Gew.-% beträgt, bezogen auf die gesamten Harzfeststoffe.

4. Überzugszusammensetzung gemäß Anspruch 3, worin das Acrylpolymer mit Carboxylgruppen durch Copolyme
risieren von 3,5 bis 90 Gew.-% eines Monomers mit einer Carboxylgruppe und von 96,5 bis 10 Gew.-% eines weiteren Monomers erhältlich ist.

5. Überzugszusammensetzung gemäß Anspruch 4, worin das Monomer mit Carboxylgruppe ein langkettiges Mono
mer mit einer endständigen Carboxylgruppe ist.

6. Überzugszusammensetzung gemäß Anspruch 5, worin das Acrylpolymer mit Carboxylgruppen durch Copolyme
risieren von 5 bis 90 Gew.-% eines Monomers mit einer Carboxylgruppe, von 95 bis 10 Gew.-% eines Monomers mit einer Hydroxylgruppe und von 0 bis 60 Gew.-% eines weiteren Monomers erhältlich ist.

7. Überzugszusammensetzung gemäß Anspruch 4, worin das Monomer mit der Carboxylgruppe durch Halb-Veres
terung eines Monomers mit einer Anhydridgruppe mit einem Monoalkohol erhältlich ist, worin das Molverhältnis der Anhydrid- zur Hydroxylgruppe 1/10 bis 1/1 beträgt.

8. Überzugszusammensetzung gemäß Anspruch 3, worin das Acrylpolymer mit Carboxylgruppen durch die Stufen einer Copolymerisation von 10 bis 40 Gew.-% eines Monomers mit einer Anhydridgruppe und von 60 bis 85 Gew.-% eines anderen Monomers und einer Halb-Veresterung des entstandenen Polymers mit Anhydridgruppen mit einem Monoalkohol erhältlich ist, worin das Molverhältnis der Anhydrid- zur Hydroxylgruppe 1/10 bis 1/1 beträgt.


10. Überzugszusammensetzung, umfassend:

\[ 20 bis 80 Gew.-\% eines ersten Polymers mit Carboxyl- und Carboxylatgruppen mit einem Säure-Wert von 30 bis 300 mg KOH/g Feststoffe und mit einem zahlen-
durchschnittlichen Molekulargewicht von 500 bis 20.000, \]

welches durch die Stufen einer Copolymerisation von 10 bis 40 Gew.-% eines Monomers mit einer Anhydrid-
gruppe und von 60 bis 90 Gew.-% eines weiteren Monomers und einer Halb-Veresterung des entstandenen Anhydridgruppen aufweisenden Polymers mit einem Monoalkohol erhältlich ist, wobei das Molverhältnis der Anhydrid- zur Hydroxylgruppe 1/10 bis 1/1 beträgt;

\[ 20 bis 80 Gew.-\% eines zweiten Polymers mit Carboxyl- und Hydroxylgruppen mit einem Säure-Wert von 30 bis 300 mg KOH/g Feststoffe, einem Hydroxyl-Äquivalentgewicht von 350 bis 1.200 und mit einem zahlen-
durchschnittlichen Molekulargewicht von 1.000 bis 8.000, welches durch Copolymerisieren von 5 bis 90 Gew.-\% \]
% eines Monomers mit einer Carboxylgruppe, von 95 bis 10 Gew.-% eines Monomers mit einer Hydroxylgruppe und von 0 bis 60 Gew.-% eines weiteren Monomers erhältlich ist;

eine Verbindung mit mindestens 2 Epoxigruppen; und

0,01 bis 3,0 Gew.-Teile, bezogen auf 100 Gew.-Teile der gesamten Harzfeststoffe, eines in Anspruch 1 definierten Oniumsalzes.


12. Überzugszusammensetzung gemäß einem der Ansprüche 1 bis 11, worin die Verbindung mit den mindestens 2 Epoxigruppen ein Epoxi-Äquivalentgewicht von 280 bis 900 und ein zählendurchschnittliches Molekulargewicht von 500 bis 50.000 aufweist.


16. Überzugszusammensetzung gemäß einem der Ansprüche 1 bis 15, worin jedes R unabhängig C_{1-20}-Alkyl, C_{5-8}-Aryl oder C_{6-10}-Aralky1, wobei R mindestens 1 Sauerstoffatom aufweisen kann, und X- ein Ion sind, das aus einem sauren Phosphat oder Phosphonat der Formel abgeleitet ist:

\[(R'O)_{3-n}PO(OH)_n\text{ oder } R'R'O-P(O)(OH)-R',\]

worin jedes R' unabhängig C_{1-20}-Alkyl, C_{6-10}-Cycloalkyl, C_{5-8}-Aryl oder C_{6-10}-Aralky1 und n eine ganze Zahl von 1 bis 3 sind.

17. Überzugszusammensetzung gemäß einem der Ansprüche 1 bis 16, worin das Oniumsalz aus Tetrabutylammonium dibutylphosphat, Trimethyl benzyl ammonium dibutylphosphat, Trimethyl benzyl ammoniumdi(2-ethylhexyl)phosphonat, Trimethylcetlylammonium dibutylphosphat, Trimethylcetlylammoniumbutylphosphonat, Tetrabutylammonium di(2-ethylhexyl)phosphat, Btrimethylbenzyl ammonium-n-butyrophosphat und aus Trimethylcetlylammonium2-ethylhexylphosphat ausgewählt ist.

18. Überzugszusammensetzung gemäß einem der Ansprüche 1 bis 17, worin die Verbindung mit den mindestens 2 Epoxigruppen aus einem Monomer erhältlich ist, ausgewählt aus Glycidyl(meth)acrylat und aus β-Methyl glycidyl (meth)acrylat.

19. Überzugszusammensetzung gemäß einem der Ansprüche 1 bis 9, worin die Verbindung mit den mindestens 2 Carboxy gruppen

(i) ein Acryl polymer, erhältlich aus einem Monomer, ausgewählt aus Glycidyl(meth)acrylat und aus β-Methyl glycidyl(meth)acrylat,

(ii) ein Glycidylether eines polyhydrischen Alkohols oder
(iii) ein Glycidylester einer polybasischen Säure

ist.

20. Verfahren zur Bildung eines gehärteten Films auf einem Substrat, wobei man:

- eine Oberfläche des Substrats grundiert oder mit einem Zwischenüberzug versieht,

- einen Wasser- oder Lösungsmittel-basierten Farb-Grundanstrich auf die grundierte und/oder mit Zwischenüberzug versehene Oberfläche aufbringt,

- eine klare Überzugszusammensetzung auf die mit dem Grundanstrich überzogene Oberfläche des Substrats aufbringt, ohne die Basisschicht zu härten, und man

sowohl die Basisschicht als auch die klare Überzugsschicht einbrennt und härtet,

worin die klare Überzugszusammensetzung eine Überzugszusammensetzung gemäß einem der vorhergehenden Ansprüche umfasst.

**Revendications**

1. Composition de revêtement transparente, à base de solvant, comprenant :

   (a) un composé ayant au moins 2 groupes carboxyle ;
   (b) un composé ayant au moins 2 groupes époxy ; et
   (c) 0,01 à 3,0 parties en poids, pour 100 parties en poids du total des matières solides de résine, d’un sel d’onium représenté par la formule :

   \[ \text{N}(\text{R})_{4\alpha}^{\pm}X^{\alpha} \]

   dans laquelle chaque symbole R est indépendamment choisi parmi des groupes alkyle en C_{1-20}, des groupes alkyle cycliques en C_{6-10}, des groupes aryle en C_{5-8} et des groupes aralkyle en C_{6-10}, ou deux R, pris ensemble, peuvent former avec l’atome N un noyau hétérocyclique saturé ou insaturé, et R peut avoir au moins un atome d’halogène, d’azote ou d’oxygène ; X représente un ion nitrite, nitrate, phosphonate ou phosphate acide, et α représente un nombre entier de 1 à 3.

2. Composition de revêtement selon la revendication 1, dans laquelle le composé ayant au moins 2 groupes carboxyle est un polymère ayant des groupes carboxyle, un indice d’acide de 30 à 300 mg de KOH/g de matières solides et une masse moléculaire moyenne en nombre de 500 à 50 000.

3. Composition de revêtement selon la revendication 2, dans laquelle le polymère ayant des groupes carboxyle est un polymère de type acrylique ou polyester ayant des groupes carboxyle, et la quantité de ce polymère dans la composition de revêtement est de 10 à 80 % en poids par rapport au total des matières solides de résine.

4. Composition de revêtement selon la revendication 3, dans laquelle le polymère de type acrylique ayant des-groupes carboxyle peut être obtenu par copolymérisation de 3,5 à 90 % en poids d’un monomère ayant un groupe carboxyle et de 96,5 à 10 % en poids d’un autre monomère.

5. Composition de revêtement selon la revendication 4, dans laquelle le monomère ayant un groupe carboxyle est un monomère à longue chaîne ayant un groupe carboxyle terminal.

6. Composition de revêtement selon la revendication 5, dans laquelle le polymère de type acrylique ayant des-groupes carboxyle peut être obtenu par copolymérisation de 5 à 90 % en poids d’un monomère ayant un groupe carboxyle, de 95 à 10 % en poids d’un monomère ayant un groupe hydroxyle, et de 0 à 60 % en poids d’un autre monomère.

7. Composition de revêtement selon la revendication 4, dans laquelle le monomère ayant un groupe carboxyle peut
être obtenu par semi-estérification d'un monomère ayant un groupe anhydride avec un monoalcool, le rapport molaire du groupe anhydride au groupe hydroxyle étant de 1/10 à 1/1.

8. Composition de revêtement selon la revendication 3, dans laquelle le polymère de type acrylique ayant des groupes carboxyle peut être obtenu par les étapes de copolymérisation de 10 à 40 % en poids d'un monomère ayant un groupe anhydride, et de 60 à 85 % en poids d'un monomère différent, et de semi-estérification du polymère résultant ayant des groupes anhydride avec un monoalcool, le rapport molaire du groupe anhydride au groupe hydroxyle étant de 1/10 à 1/1.

9. Composition de revêtement selon la revendication 3, dans laquelle le polymère de type acrylique ayant des groupes carboxyle peut être obtenu par les étapes de copolymérisation de 3,5 à 45 % en poids d'un monomère ayant un groupe carboxyle, de 10 à 40 % en poids d'un monomère ayant un groupe anhydride, le complément étant formé d'un autre monomère, et de semi-estérification du polymère résultant ayant des groupes anhydride avec un monoalcool, le rapport molaire du groupe anhydride au groupe hydroxyle étant de 1/10 à 1/1.

10. Composition de revêtement comprenant:

20 à 80 % en poids d'un premier polymère ayant des groupes carboxyle et des groupes carboxylate, un indice d'acide de 30 à 300 mg de KOH/g de matières solides et une masse moléculaire moyenne en nombre de 500 à 20 000, et qui peut être obtenu par les étapes de copolymérisation de 10 à 40 % en poids d'un monomère ayant un groupe anhydride et de 60 à 90 % en poids d'un autre monomère, et de semi-estérification du polymère résultant ayant des groupes anhydride avec un monoalcool, le rapport molaire du groupe anhydride au groupe hydroxyle étant de 1/10 à 1/1 ;

20 à 80 % en poids d'un second polymère ayant des groupes carboxyle et des groupes hydroxyle, un indice d'acide de 30 à 300 mg de KOH/g de matières solides, un poids équivalent d'hydroxyle de 350 à 1200 et une masse moléculaire moyenne en nombre de 1000 à 8000, et qui peut être obtenu par copolymérisation de 5 à 90 % en poids d'un monomère ayant un groupe carboxyle, de 95 à 10 % en poids d'un monomère ayant un groupe hydroxyle, et de 0 à 60 % en poids d'un autre monomère ;

un composé ayant au moins 2 groupes époxy ; et

0,01 à 3,0 parties en poids, pour 100 parties en poids du total des matières solides de résine, d'un sel d'onium tel que défini dans la revendication 1.

11. Composition de revêtement selon la revendication 6 ou la revendication 10, dans laquelle le monomère ayant un groupe carboxyle est un monomère à longue chaîne ayant un groupe carboxyle terminal, et le monomère ayant un groupe hydroxyle est un monomère à longue chaîne ayant un groupe hydroxyle terminal.

12. Composition de revêtement selon l'une quelconque des revendications 1 à 11, dans laquelle le composé ayant au moins 2 groupes époxy présente un poids équivalent d'époxy de 280 à 900 et une masse moléculaire moyenne en nombre de 500 à 50 000.

13. Composition de revêtement selon la revendication 12, dans laquelle le composé ayant au moins 2 groupes époxy est un polymère de type acrylique ayant des groupes époxy, un éther de glycidyle d'un polyol ou un ester de glycidyle d'un acide polyfonctionnel, et la quantité de ce composé dans la composition est de 20 à 80 % en poids du total des matières solides de résine.

14. Composition de revêtement selon la revendication 13, dans laquelle le polymère de type acrylique ayant des groupes époxy peut être obtenu par copolymérisation de 10 à 60 % en poids d'un monomère ayant un groupe époxy et de 90 à 40 % en poids d'un autre monomère.

15. Composition de revêtement selon la revendication 13 ou la revendication 14, dans laquelle le polymère de type acrylique ayant des groupes époxy a également des groupes hydroxyle, un poids équivalent d'époxy de 280 à 900, un poids équivalent d'hydroxyle de 280 à 1200 et une masse moléculaire moyenne en nombre de 500 à 50 000, et dans laquelle le polymère de type acrylique peut être obtenu par copolymérisation de 10 à 60 % en poids d'un monomère ayant un groupe époxy, de 5 à 60 % en poids d'un monomère ayant un groupe hydroxyle, le complément étant formé d'un autre monomère.

16. Composition de revêtement selon l'une quelconque des revendications 1 à 15, dans laquelle chaque symbole R représente indépendamment un groupe alkyle en C1-20, un groupe aryle en C5-8 ou un groupe aralkyle en C6-10.
et R peut avoir au moins un atome d’oxygène, et X⁻ représente un ion dérivé d’un phosphonate ou d’un phosphate acide de formule

$$(R'O)^{3-n}PO(OH)_n \text{ ou } R'R'O-P(O)(OH)-R'$$

dans laquelle chaque symbole R' représente indépendamment un groupe alkyle en C_{1-20}, un groupe cycloalkyle en C_{6-10}, un groupe aryle en C_{5-8}, et un groupe aralkyle en C_{6-10}, et n représente un nombre entier de 1 à 3.

17. Composition de revêtement selon l’une quelconque des revendications 1 à 16, dans laquelle le sel d’onium est choisi parmi le dibutylphosphate de tétrabutylammonium, le dibutylphosphate de triméthylbenzylammonium, le di(2-éthylhexyl)-phosphonate de triméthylcétylammonium, le butylphosphonate de triméthylcétylammonium, le di(2-éthylhexyl)-phosphate de tétrabutylammonium, le n-butylphosphate de triméthylbenzylammonium, et le 2-éthylhexylphosphate de triméthylcétylammonium.

18. Composition de revêtement selon l’une quelconque des revendications 1 à 17, dans laquelle le composé ayant au moins 2 groupes époxy peut être obtenu à partir d’un monomère choisi parmi le (méth)acrylate de glycidyle et le (méth)acrylate de β-méthylglycidyle.

19. Composition de revêtement selon l’une quelconque des revendications 1 à 9, dans laquelle le composé ayant au moins 2 groupes carboxyle est

(i) un polymère de type acrylique pouvant être obtenu à partir d’un monomère choisi parmi le (méth)acrylate de glycidyle et le (méth)acrylate de β-méthylglycidyle,

(ii) un éther de glycidyle d’un polyol ou

(iii) un ester de glycidyle d’un acide polyfonctionnel.

20. Procédé de formation d’un film durci sur un substrat, comprenant les étapes consistant à :

revêtir d’une couche de fond ou d’une couche intermédiaire une surface du substrat ;

appliquer une peinture de base de couleur, aqueuse ou à base de solvant, sur la surface revêtue d’une couche de fond ou d’une couche intermédiaire ;

appliquer une composition de revêtement transparente sur la surface de base revêtue du substrat, sans faire durcir la couche de base ; et

faire cuire et durcir à la fois la couche de base et la couche de revêtement transparente ;

dans laquelle la composition de revêtement transparente comprend une composition de revêtement selon l’une quelconque des revendications précédentes.